

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 378 893
A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89303040.3

(51) Int. Cl.⁵: A23D 9/00

(22) Date of filing: 28.03.89

(30) Priority: 17.01.89 JP 8151/89

(43) Date of publication of application:
25.07.90 Bulletin 90/30

(84) Designated Contracting States:
CH DE ES FR GB LI NL

(71) Applicant: Kao Corporation
14-10, Nihonbashi Kayabacho 1-chome
Chuo-Ku Tokyo 103(JP)

(72) Inventor: Yasukawa, Takuji
8762-23, Doaihoncho 1-chome
Hazaki-cho Kashima-gun Ibaraki(JP)
Inventor: Yasumura, Daisuke
8762-23, Doaihoncho 1-chome
Hazaki-cho Kashima-gun Ibaraki(JP)
Inventor: Yamasawa, Kimiko
9809-6, Doaihoncho 4-chome
Hazaki-cho Kashima-gun Ibaraki(JP)
Inventor: Tanaka, Yukitaka
8762-23, Doaihoncho, 1-chome
Hazaki-cho Kashima-gun Ibaraki(JP)
Inventor: Nishide, Tsutomu
8762-23, Doaihoncho, 1-chome
Hazaki-cho Kashima-gun Ibaraki(JP)

(74) Representative: Bannerman, David Gardner et
al
Withers & Rogers 4 Dyer's Buildings Holborn
London, EC1N 2JT(GB)

(54) Edible oil/fat compositions.

(57) An edible oil and fat composition comprises a phospholipid and a glyceride mixture comprising 5 to 100 percent by weight of a diglyceride. The phospholipid is a decomposition product of natural lecithin. It is stable and suitable for food and a cooking oil.

EP 0 378 893 A2

Edible oil/fat compositions

BACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to edible oil/fat compositions (the term "oil/fat composition(s)" shall mean composition(s) containing oil and/or fat as principal component and other desired components herein), and more particularly to edible oil/fat compositions comprising a diglyceride-containing glyceride mixture and a
10 phospholipid having a specified composition, and thus having advantages of good stability against oxidation and heat which may occur by cooking, for example, deep- and pan-frying, roasting, and baking, and of providing little greasy or oily distastefulness and no sitting heavy in the stomach when taken in such raw state as contained in dressing, mayonnaise, or the like.

15 Description of the prior Art

In these days are used various edible oils most of which includes soybean oil, rapeseed oil, corn oil, cotton seed oil, sunflower oil, and sesame oil, alone respectively, or in combination, in the
20 form of mixture or composition. More recently, there is tendency of liking light or soft taste and flavor (referred to as taste/flavor hereinafter) rather than heavy or rich food. Because of being difficult to mix with digestive juice compared with other essential nutrients such as proteins and carbohydrates, however fats and oils tend to stay over longer time in the digestive tract, and this is considered a cause for physiological discomforts such as sitting heavy in the stomach by taking much greasy or oily food, while they are very
25 important for making the taste and appearance better. An actual problem with oils and fats therefore resides in incompatibility between their effect which may cause physiological discomforts, such as greasy distastefulness and sitting heavy in the stomach, and their improving effect on the taste/flavor and appearance.

In addition, edible oils and fats plays important parts for cooking from the aspect of function, for
30 example, in order to prevent food material from burning and sticking to cooking utensils, baking molds, top plates, for instance, on baking cakes or breads, and frying in a pan.

On the other hand, there are so far a number of surface active agents as mold-releasing agents for use in cooking, for example, baking sponge cakes or frying eggs, so as to prevent doughs or eggs from burning and sticking, and above all lecithins are known as specifically effective for this purpose. Thus vegetable oils
35 containing lecithin(s) added thereto are used as mold releasing oils. Lecithins have also anti-spattering effect for cooking, and for this reason, lecithin-added oils are on the market as "reduced-spattering oil for roasting on iron plate".

The term "lecithins" refers herein to phospholipid mixtures containing as major gradients phosphatidyl choline, phosphatidyl ethanolamine, and so on. Typical lecithins are yielded from soybean or egg yolk by
40 extraction and purification.

Natural lecithins including lecithins from soybean and egg yolk are labile and, even if protected by oil or fat, turn black brown (browning phenomenon) as the result of heating. The decomposition and denaturation products give out bad smell and offensive odor, resulting in impairment in taste/flavor of food. For this reason, the uses and amounts of lecithins are limited at present situation. For the purpose of overcoming
45 the difficulty with respect to lecithins, some approaches have been made, for example modification, such as hydroxylation, of lecithins (U.S. patent 3 661 605), and the use of specified HLB lecithins (U.S. patent 3 896 975). Japanese patent publication B 61-48520, Japanese patent publication A 54-126 206 and Japanese patent publication A 54-127 408 disclose the use of mixtures of lecithin with salts of organic acids and amino acids. The problem is not substantially solved.

50

SUMMARY OF THE INVENTION

Presently-used edible oils, such as salad oil are, comprise as major constituents triglycerides each

being an ester of three fatty acids and a glycerol, though their fatty acids are different with source oils. Triglycerides is subjected to hydrolysis by the action of digestive enzymes in the digestive tract to be converted into glycerides greater in polarity (high hydrophilic), that is, di- and monoglycerides, and after all probably absorbed through the epithelial cells of the small intestine, (A.P.Hofmann & B. Borgstroem ('64), J. Clin. Invest. 43(8), 24).

The inventors made detailed study on glyceride mixtures and to our surprise have found out that when a specified glyceride, i.e. diglyceride, is contained in them, substantially more oil intake with them than that with common salad oils induced no peculiar sitting heavy in the stomach which might occur after taking much greasy or oily dish while they have similar properties to those of common salad oils, and can be used well conveniently as oils for general cooking. In addition, it was to our surprise found out that dishes containing such edible oil/fat compositions even in considerably much amount gave little oily distastefulness. Thus they may be said to be edible oils appropriate for fashion of taste in these days.

The inventors made further study on improvement in shortcomings of the afore-said conventional oils for cooking, for instance, smoking on heating and unwanted taste and flavor, thus to provide satisfactory edible oil compositions for cooking.

In our further study, it was demonstrated as described above that the major constituents of natural lecithins (such as soybean lecithin and egg yolk lecithin), which were nitrogen-containing compounds of phospholipids, such as phosphatidyl choline (PC) and phosphatidyl ethanolamine (PE), are so heat labile as to readily get colored and give out bad smell on heating. In addition it was found out that treatment of these natural lecithins with enzymes such as phospholipase D and Phospholipase A₂, fractionation, and so on, to reduce contents of PC and PE and on the other hand increase the contents of phosphatidic acid (PA), lysophosphatidic acid (LPA), phosphatidyl glycerol (PG), and phosphatidyl inositol (PI) to specified or higher level, resulted in markedly reduced getting-colored and giving-out of bad smell while still keeping the good mold-releasing effect and superior anti-spattering effect. In this way the present invention has been accomplished.

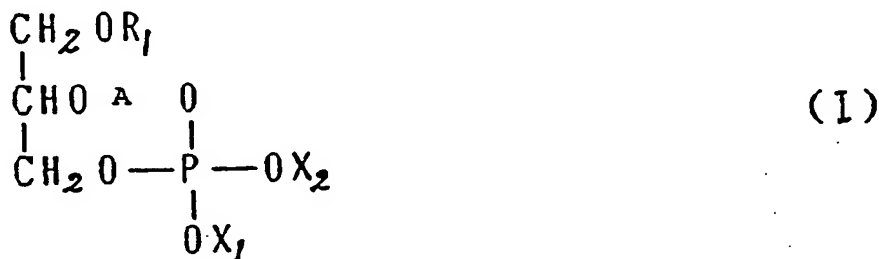
An edible oil and fat composition of the invention comprises a phospholipid and a glyceride mixture comprising 5 to 100 percent by weight of a diglyceride. It is preferred that the composition comprises 0.1 to 30 percent by weight of a phospholipid and 20 to 99.9 percent by weight of a glyceride mixture comprising 5 to 100 percent by weight of a diglyceride.

A preferable phospholipid is a decomposition product of natural lecithin. It is stable and suitable for food and a cooking oil.

The phospholipid to use in the invention has a lower nitrogen content than its raw material including choline, ethanolamine and serine. It is prevented on use from coloring, fuming and badly smelling.

It is preferable that the phospholipid is a product mixture obtained by decomposing natural lecithin with use of an enzyme.

A preferable phospholipid has the below shown formula (I) in which A is hydrogen or R₂, R₁ and R₂ each are an aliphatic acyl group, saturated or unsaturated, having 8 to 24 carbon atoms, X₁ is selected from the group consisting of base residues of choline, ethanolamine, serine, inositol and glycerol, hydrogen, an alkali metal, an alkaline earth metal, a trivalent metal and ammonium, and X₂ is selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, a trivalent metal and ammonium and the phospholipid has a weight ratio of the phospholipid having no nitrogen in X₁ and X₂ to the phospholipid having nitrogen in X₁ and X₂ at a value of 1.0 or more.



Preferred phospholipids includes PA (X₁ is hydrogen and X₂ is hydrogen), a salt thereof, LPA (X₁, X₂ and A are hydrogen), a salt thereof, PG (X₁ is hydrogen and X₂ is -CH₂CHOHCH₂OH) and PI (X₁ is hydrogen and X₂ is inositol).

A more preferable phospholipid has a weight ratio of nitrogen to phosphorus in the range between zero and 0.20.

Another preferable phospholipid contains phosphatidic acid (PA) and/or a phosphatidic acid salt and lysophosphatidic acid (LPA) and/or a lysophosphatidic acid salt and a weight ratio of the sum total of the phosphatidic acid, a salt thereof, lysophosphatidic acid and a salt thereof to the sum total of phosphatidyl choline (PC) and phosphatidyl ethanolamine (PE) at a value of 1.0 or above.

5 The glyceride to use in the invention has aliphatic acid residues having 8 to 24 carbon atoms, being either saturated or unsaturated, straight or branched. A straight one, saturated or unsaturated, is preferable.

A preferable glyceride mixture comprises from 5 to 99.9 percent by weight of the diglyceride.

It is preferable that

(a) the glyceride mixture comprises monoglycerides, diglycerides and triglycerides,

10 (b) a weight ratio of the diglyceride to the monoglyceride ranges from 5:1 to 990:1 and

(c) the aliphatic acid (acyl) moieties in the glycerides have 8 to 24 carbon atoms.

It is more preferable that in addition to the above (a), (b) and (c), the aliphatic acid moiety comprises 70 percent by weight or above of unsaturated aliphatic acid moieties and

15 (d) the diglycerides contains 40 percent by weight or lower of diglycerides having unsaturated and saturated aliphatic acid moieties and 5 percent by weight or lower of diglycerides having two saturated aliphatic acid moieties or 70 wt.% or less of unsaturated aliphatic acid moieties.

Instead of the above preferable requirement (d), (d') the diglycerides contains 40 percent by weight or more of diglycerides having unsaturated and saturated aliphatic acid moieties and 5 percent by weight or more of diglycerides having two saturated aliphatic acid moieties.

20 The composition may further comprise 0.1 to 50 percent by weight of ethyl alcohol.

Detailed Description of the Invention

25 It therefore is the principal object of the present invention to provide edible oil/fat compositions comprising in combination a diglyceride-containing mixture and a phospholipid of a specified composition, and having superior characteristics of by no means leaving greasy or oily distastefulness behind after meal, and of having good mold-releasing effect and superior anti-spattering effect, and being confined to markedly reduced getting colored and giving-out of bad smell resulting from heating.

30 Phospholipids according to the present invention can be obtained, for example, by two methods described in the following, though not limited to these. The first: natural lecithins typically such as soybean lecithin, are subjected to the action of catalyst such as phospholipase D or A₂ to decompose selectively phosphatidyl choline and phosphatidyl ethanolamine, thus contents of these being reduced, and at the same time to increase the contents of phosphatidic acid and/or of its salts with alkali metal, alkaline earth metal, trivalent metal and ammonium radical, and the contents of lysophosphatidic acid and/or of its salts with alkali metal, alkaline earth metal, trivalent metal and ammonium radical. The second: natural lecithins are subjected to transphosphatidilation in the presence of a catalyst, phospholipase D, to reduce the contents of phosphatidyl choline (PC), phosphatidyl ethanolamine (PE), and phosphatidyl serine (PS), and increase phosphatidyl glycerol (PG) and phosphatidyl inositol (PI) in the lecithins.

40 Suitable phospholipids for use in the present invention are those containing phosphatidic acid and/or its salt and lysophosphatidic acid and/or its salt in a ratio of 1.0 or more to the summed content of phosphatidyl choline and phosphatidyl ethanolamine.

Free phosphatidic acid and also its salts can be used in the present invention, and the suitable salts include alkali metal salts such as sodium phosphatidate and potassium phosphatidate; alkaline metal salts 45 such as calcium phosphatidate and magnesium phosphatidate; trivalent metal salts such as aluminum phosphatidate; and ammonium phosphatidate; and monovalent metal (such as sodium and potassium) salts are especially favorable. Suitable fatty acids as constituents of phosphatidic and lysophosphatidic acids include saturated or unsaturated fatty acids having 6 to 20 carbon atoms, and unsaturated fatty acids having 16 to 18 carbon atoms are the most favorable.

50 Phosphatidic and/or lysophosphatidic acids may be used alone and as mixtures of them. It however is favorable to use phospholipids in which other phosphatidyl choline and phosphatidyl ethanolamine, etc., are not all separated and remain, and the content of phosphatidic acid and/or lysophosphatidic acid is 1.0 or more to the summed content of phosphatidyl choline and phosphatidyl ethanolamine, and among all the summed remaining content is 0.01 to 20% by weight in the phospholipids because the use of these 55 phospholipids for cooking effects reduction of oily distastefulness and better taste/flavor.

Suitable phospholipids containing PG and PI for use in the present invention are of composition in which N/P ratio ranging from 0 to 0.20, and the weight ratio of PG + PI to PC + PE + PS is 1.0 or more.

Suitable fatty acids as constituents of phospholipids containing PG and PI are of the types as described

above. Phospholipids having the types of fatty acids can be yielded from vegetable seed-derived lecithins, especially those derived from soybean, rapeseed and sunflower.

Besides it is suitable to handle the above-mentioned content of phospholipids as the content of acetone-insoluble matter, which can be regarded as a criterion of total phospholipid and is determined in accordance with the determination of lecithin content as directed in "the Japanese Standards of Food Additives".

The invention includes an embodiment of an edible oil and/or fat which meet the following chemical composition requirements.

- (a) the weight ratio of diglycerides to monoglycerides is within the range of 5:1 to 990:1;
- (b) the content of diglycerides in whole oil is within the range of 5 to 100% by weight, favorably 8 to 80% by weight;
- (c) the fatty acid residues of mono-, di- and triglycerides have each 8 to 24 carbon atoms.

A more preferred requirement is:

The invention includes an embodiment of an edible oil and/or fat which meet the following chemical composition requirements.

- (a) the weight ratio of diglycerides to monoglycerides is within the range of 5:1 to 990:1;
- (b) the content of diglycerides in whole oil is within the range of 5 to 100% by weight, favorably 8 to 80% by weight;
- (c) the fatty acid residues of mono-, di- and triglycerides have each 8 to 24 carbon atoms, and the content of unsaturated fatty acid residues amounts to 70% by weight or more of the content of the fatty acid residues; and

(d) the content of diglycerides having in combination a saturated acid and an unsaturated fatty acid is up to 40% by weight, the content of diglycerides having in combination two saturated fatty acids is up to 5% by weight, and the content of diglycerides having in combination two unsaturated fatty acids is the rest.

Smaller content of diglycerides than 5% by weight makes the solubility of the phospholipid insufficient. High content of diglycerides in combination with high content of monoglycerides in the glycerides mixture have a tendency to give out smoke on heating, and thus suitable content of diglycerides is within the range of 8 to 80% by weight. Like diglycerides, monoglycerides have effect to increase the solubility of phospholipids. Unlike diglycerides, however monoglycerides, even in low content (if higher than 10% by weight) in oil phase, are involved in giving out much smoke on heating. Accordingly the content of monoglycerides in monoglyceride mixture should be up to 10% by weight, favorably up to 2% by weight.

Although butter, shortenings, lard, or the like are used extensively as edible oil/fat compositions, as described above, new edible oil/fat compositions meeting the aforesaid requirements with respect to cooking characteristics (stability against oxidation) and digestion characteristics (produce no oily distastefulness) is still desired to great extent in the present situation.

As appropriate for such desire is provided the oils and fats according to the present invention having in glyceride composition the following features:

- (a) Weight ratio of diglycerides to monoglycerides is within the range of 5:1 to 990:1;
- (b) The content of diglycerides in whole oil is within the range of 5 to 100% by weight;
- (c) the fatty acid residues of diglycerides have 8 to 24 carbon atoms, and
- (d) the content of diglycerides having in combination a saturated acid and an unsaturated fatty acid is 40% by weight or higher, the content of diglycerides having in combination two saturated fatty acids is 5% by weight or higher, and the content of diglycerides having in combination two unsaturated fatty acids is the rest.

Suitable glyceride mixture for use in the present invention include oils or fats having a elevated content of diglycerides yielded either by the interesterification of the mixture of glycerol with at least one oil or fat having high content of unsaturated fatty acid residues selected from the group consisting of safflower oil, olive oil, cottonseed oil, rapeseed oil, corn oil, soybean oil, palm oil, rice (bran and germ) oils, sunflower oil, sesame oil, lard, beef tallow, fish oil, butter, and fractionated, randomized and interesterified oils of them, or by the esterification of glycerol with unsaturated fatty acids derived from the oils or fats; and also include mixtures of the yielded oils or fats having a elevated content of diglycerides with the above-mentioned raw oils or fats.

Surplus monoglycerides produced by the interesterification or esterification can be removed by molecular distillation or chromatography. Although these reactions can be accomplished by other chemical reactions by the use of alkaline catalyst, or the like, it is favorable for yielding edible oils having good taste and flavor according to the invention that the reaction is made under moderate conditions, for example, with enzyme such as 1- and 3-site selective lipase.

Another process for increasing the content of diglycerides in glyceride mixture is, for example, to use

fractionated oils from natural edible oils. This process is appropriated for natural oils or fats having relative high content of unsaturated fatty acids because the recovery of lower melting point fractions results in such improvement in resistance to cooling and in such increase in the content of diglycerides in the oils or fats as satisfactorily usable in the present invention.

Preferred edible oil/fat compositions according to the invention are obtained by blending the aforesaid edible oils or fats warmed to 60° to 80° C, with 0.1 to 30% by weight, favorably 0.3 to 20% by weight of a phospholipid containing PA, LPA and/or salts of these, PG or PI, LPG or LPI.

To the edible oil/fat compositions according to the invention are allowed, for the purpose of improving preventive effect on burning and sticking, anti-spattering effect, and emulsifying effect for the preparation of dressings or mayonnaises, to add various types of emulsifiers such as sucrose fatty acid esters, sorbitan fatty acid esters, propylene glycol fatty acid esters, organic acid monoglycerides, polyglycerin fatty acid ester, etc. Also it is allowed to add various antioxidants, seasonings or flavors, nutrient-fortifiers, consistency-reducing agent, etc.

A further feature of the edible oil/fat according to the invention is to have good solubility for such sparingly soluble emulsifiers as insoluble or becoming insoluble and thus separating in common oils as time passes.

The edible oil/fat compositions according to the present invention has advantages of having good mold releasing effect and superior anti-spattering effect, and good taste and flavor, and causing by heating neither to getting colored nor giving out bad smell, and thus having very extensive uses. They can be easily digested through light work of the digestive tract, and contribute to not greasy, dry taste. Accordingly they are appropriate for the fashion of disliking greasy taste in these days while there is a tendency of the intake of oil to be increasing.

In the invention, a liquid alcohol such as ethyl alcohol and glycerol may be added to the composition to obtain an edible oil and fat composition of the spraying.

Examples

The invention will be described more fully for making clearer the effects of it by way of Examples by which the invention is not limited.

Moreover "%" means % by weight unless otherwise specified.

Reference Examples 1 to 3

With vegetable oils shown in Table 1 as source oils, diglyceride mixtures 1 through 3 shown in Table 1 were obtained in the following procedure: The fatty acid (860g) yielded from a vegetable oil under the action of a commercially available preparation of fixed 1- and 3-position selective lipase (Trade mark: Lipozyme 3A; Novo Industry A.S.) was allowed to react with glycerin (140g) at 40° C. After completion of reaction, reaction product was filtered to remove the used lipase, subjected to molecular distillation, and purified according to normal method with a yield of diglyceride mixture.

Table 1

| Diglyceride mixtures | | | | |
|--------------------------------------|------|--------------|----------|-------------|
| Ref. Ex. No. | | 1 | 2 | 3 |
| Source | | Rapeseed oil | Corn oil | Soybean oil |
| Composition ⁴⁾ (%) | TG1) | 18 | 15 | 68 |
| | DG2) | 80 | 70 | 85 |
| | MG3) | 2 | 15 | 2 |
| Unsaturated fatty acid content(%) | | 92.8 | 85.1 | 85.9 |
| Notes: | | | | |

1) TG : Triglyceride

2) DG : Diglyceride

3) MG : Monoglyceride

4) Figures indicate contents(%) through gas chromatography

Examples 1 to 6

To each of diglyceride mixtures yielded Reference Examples 1 to 3 and given in Table 1 were added a vegetable oil and a lecithin, and mixed to prepare edible oils, of which glyceride compositions and in which contents of unsaturated fatty acids are summarized in Table 2.

Fatty acid compositions of phospholipids are given in Table 3.

Table 2. Glyceride compositions and storage stabilities of cooking oil compositions

(A)

| | Product of the invention (Example No.) | | | | |
|---|--|---------------------|---------------------|---------------------|---------------------|
| | 1 | 2 | 3 | 4 | 5 |
| Glyceride mixture* No. (parts) | (20) | (50) | (80) | (50) | (25) |
| Edible oil or fat (parts) | Safflower oil (80) | Corn oil (50) | Corn oil (20) | Soybean oil (50) | Cotton-oil (75) |
| Glyceride 4) composition (%) | TG1) 84.6 DG2) 15.0 MG3) 0.4 | 59.0 40.0 1.0 | 33.4 65.0 1.6 | 57.5 35.5 7.0 | 79.9 19.8 0.3 |
| Content of unsaturated fatty acid (%) | 50.0 | 86.3 | 90.8 | 85.2 | 76.0 |
| Phospholipid sample No. (See Table 3)5) | 2 | 3 | 4 | 5 | 5 |
| State after 3 months' storage at 20°C | Uniform Good | Uniform Good | Uniform Good | Uniform Good | Uniform Good |

(B)

| | | Comparative product | | | |
|--|----------------------|---------------------|------------------------------------|------------------------------------|------------------------------------|
| | | 6 | 1 | 2 | 3 |
| Glyceride mixture* No. (parts) | | 3 (100) | - | - | - |
| Edible oil or fat (parts) | | - | Safflower oil (100) | Corn oil (100) | Cotton (100) |
| Glyceride4) composition (%) | TG1) DG2) MG3) | 63.0 35.0 2.0 | 98.9 1.0 0.1 | 99.1 0.8 0.1 | 99.4 0.5 0.1 |
| Content of unsatu- rated fatty acid (%) | | 85.9 | 86.4 | 84.8 | 76.1 |
| Phospholipid sample No. (See Table 3)5) | | 5 | 1 | 3 | 5 |
| State after three months storage at 20°C | | Uniform Good | Phospho- lipid Pre- cipitate | Phospho- lipid Pre- cipitate | Phospho- lipid Pre- cipitate |

* : Diglyceride mixture yielded Reference Examples 1 to 3.
 1) TG: Triglyceride 2) DG: Diglyceride 3) MG: Monoglyceride
 4) Figures (%) indicate values through chromatography.

5) Each phospholipid is added to diglyceride mixtures and edible oils by 5.0 wt. %.

| Fatty acid composition of diglycerides | | | | | | |
|--|----------|------|----------|------|---------|---------|
| Example No. | 1 | 2 | 3 | 4 | 5 | 6 |
| SS(%) | 0.2 | 0.8 | 0.2 | 0.9 | 1.0 | 0.9 |
| SU(%) | 13.5 | 20.4 | 14.3 | 19.3 | 22.3 | 23.1 |
| UU(%) | 86.3 | 78.8 | 83.4 | 82.8 | 76.7 | 76.0 |
| Diglyceride | 1 | 2 | 1 | 2 | 3 | 3 |
| mixture (from Table 1) | rapeseed | corn | rapeseed | corn | soybean | soybean |

Table 3

| Compositions of phospholipid mixtures | | | | | |
|---------------------------------------|------------------|------|--------------------|--------------------|------|
| Sample No. | 1 | 2 | 3 | 4 | 5 |
| Source | Soybean lecithin | | | | |
| Acetone-insoluble matter1) (%) | 95.9 | 97.2 | 96.8 | 96.2 | - |
| PC content2) (%) | 21.7 | 12.5 | 3.0 | 1.1 | 0.0 |
| PB content3) (%) | 18.8 | 16.0 | 12.5 | 3.6 | 0.1 |
| PA + LPA content4) (%) | 12.9 | 25.3 | 48.7 ⁵⁾ | 58.6 ⁶⁾ | 98.9 |
| Notes: | | | | | |

1) Acetone-insoluble matter Determined in accordance with the determination of lecithin content as directed in "the Japanese Standards of Food Additives".

2) PC (phosphatidyl choline) content (wt.%) determined according to Journal of the Japan Oil Chemist's Society (Yukagaku), 35(12), 1018-1024, 1988, taking PC molecular weight as 773.

3) PE (phosphatidyl ethanolamine) content (wt.%) determined according to the above (2), taking PE molecular weight as 728.

4) PA (phosphatidic acid) and LPA (lysophosphatidic acid) content (wt.%) determined according to the above (2), taking molecular weights of PA and LPA as 704 and 444, respectively.

5) Mixture of PA (48.6%) and LPA (0.1%)

6) Mixture of PA (55.6%) and LPA (1.0%)

With oils obtained in Examples and Comparative Examples, chow meins and French dressings were made, and organoleptic tests of them for taste/flavor and "sitting heavy in the stomach" were carried out by 30 panel members. The obtained results were summarized in Table 4.

Table 4. Organoleptic function of chow mein and French dressing

| Used oil or fat | Chow mein#1 | | French dressing#2 Light taste/ flavor#5 |
|-----------------|--------------------------|---|---|
| | Light taste/ flavor#3 | Sitting heavy in the stomach after meal#4 | |
| Example 1 | 4.2 | 0/30 | 4.5 |
| Example 2 | 4.1 | 1/30 | 4.3 |
| Comp. Exmp. 1 | 1.4 | 18/30 | 2.1 |
| Comp. Exmp. 2 | 1.4 | 22/30 | 1.8 |

Notes:

Comp. Exmp. = Comparative example

#1. Chow mein each serving

Pork 50g, cabbage 50g, bamboo shoot 25g, onion 25g, Japanese mushroom (Chochinellus shiitake) 15g, oil 30g, and Chinese noodles 180g

#2. French dressing

Oil 180g, wine vinegar 100g, salt, and pepper

This French dressing 50g was applied to 30g of shredded cabbage, and then test was made.

#3. and #4. Taste/flavor and sitting heavy on the stomach

Each panel member took chow mein (one portion) without leaving, and taste/flavor was evaluated directly after meal, and whether or not sense sitting heavy on the stomach during 4 hours.

The evaluations were made using the following 5-grade scale of lightness: 5 = Marked, 4 = Moderate, 3 = Questionable, 2 = Little and 1 = No. The results were indicated as average value of scores by 30 panel members in Table 2.

Evaluation of sitting heavy in the stomach was made on whether "Yes" or "No", and N/30 (where N is the number of "Yes") was indicated in Table 2. The evaluation was made of one sample

every day.

#5. Taste/flavor

Each panel member took the cabbage on which French dressing was spread (one portion) without leaving, and taste/flavor (sitting light in the stomach) was evaluated in the same way as in the evaluation of chow mein.

Reference Examples 4 and 5

Fatty acids (860g) yielded from rapeseed oil under the action of a commercially available preparation of fixed 1-and 3-site selective lipase (Trade mark: LiPozyne 3A; Novo Industry A.S.) was allowed to react with glycerin (140g) at 40°C for 10 hours. After completion of reaction, the reaction product was filtered to remove the used lipase, subjected to molecular distillation, and purified according to normal procedure with a yield of an oil (A) which has a composition: monoglyceride 2.0%, diglyceride 80.0%, triglyceride 18.0%.

and the proportion of unsaturated fatty acids to total fatty acids in the sum of these glycerides 89.3%.

The yielded oil (A) was mixed with rapeseed oil and safflower oil, respectively, to prepare edible oils which are indicated in Table 5 as Reference Example 4 and 5 having compositions. Table 5 shows glyceride compositions and unsaturated fatty acid contents of these oils and rapeseed oil and safflower oil for comparison.

Table 5. Compositions of edible oils

| Sample No. | Content | Glyceride composition (%) | | | Unsaturated fatty acid content (%) |
|-------------------|---|---------------------------|------|------|------------------------------------|
| | | MG#1 | DG#2 | TG#3 | |
| Ref. Example No.4 | Oil/fat (A):rapeseed oil (3:2 ratio by weight)-mixed oil | 1.2 | 50.3 | 48.5 | 87.6 |
| Ref. Example No.5 | Oil/fat (A):safflower oil (3:2 ratio by weight)-mixed oil | 1.1 | 31.3 | 67.6 | 91.8 |

Notes: #1. MG: Monoglyceride

#2. DG: Diglyceride

The composition is as follows:

SS (Sum of glycerides each having saturated fatty acid only as constituents of them) 0.2%,

SU (Sum of glycerides each having saturated and unsaturated fatty acids as constituents of them) 13.5%, and

UU (Sum of glycerides each having unsaturated acid only as constituents of them) 86.3%.

#3. TG: Triglyceride

Examples 7 and 8

Transphosphatidilation between soybean lecithin and glycerol was made in the presence of phospholipase, and of the obtained phospholipid mixtures (compositions of which are indicated in Table 6), each (2g) was dissolved in previously warmed (80° C) edible oils prepared in Reference Examples 4 and 5, respectively, (100g), and then sharply cooled to obtain pasty oil/fat compositions (Examples 7 and 8. High purity soybean lecithin (acetone insoluble matter 95% or more) 2g was used, and a pasty shortening (Comparative Example 4) were prepared in the same procedure.

Cooking tests of these oil/fat compositions were carried out with an iron frying pan for evaluation of them, and the obtained results are shown in Table 7.

Table 6

| Compositions of phospholipid mixers used in Examples 7 and 8 and high purity soybean lecithin used in Comparative Example 4 | | | |
|--|-----------|-----------|--------------|
| Component | Content | | |
| | Example 7 | Example 8 | Com. Exmp. 4 |
| PC ¹ | 3.3 | 0.5 | 23.3 |
| PE ¹ | 10.1 | 2.8 | 21.0 |
| PI ¹ | 13.4 | 15.3 | 8.5 |
| PG ¹ | 22.9 | 28.3 | 0 |
| PA ¹ | 16.0 | 19.5 | 9.3 |
| PS ¹ | 0 | 0 | 0 |
| PA + PG + PI/PC + PE + PS | 3.9 | 21.0 | 0.38 |
| N/P ² | 0.07 | 0.02 | 0.27 |
| NOTES: | | | |
| In Table 6, the following acronyms are used PC phosphatidyl choline, PE phosphatidyl ethanolamine, PI phosphatidyl inositol, PG phosphatidyl glycerol, PA phosphatidic acid, and PS phosphatidyl serine, respectively. | | | |

1) Contents of PC, PE, PI, PG, PA and PS: Determined according to Journal of the Japan Oil Chemist's Society (Yukagaku), 35(12), 1018-1024, 1986, taking molecular weights as PC 773, PE 728, PI 866, PG 778, PA 704 and PS 791, respectively

2) P and N were determined by the phosphomolybdic acid method and Kjeldahl method, respectively.

Table 7

| N and P contents of O/F compositions yielded in Examples 7 and 8 and Comparative Example 4, and evaluation results of dishes | | | |
|--|-----------|-----------|----------------------------|
| Constituent | Example 7 | Example 8 | Comp. Exmp. 4 |
| Evaluation of dishes (frizzled rice) ³⁾ | | | |
| Burned | Little | No | Yes |
| Heating-smelled | No | No | Yes, badly |
| Spattered | No | No | A little |
| Colored | Little | No | Markedly |
| Taste/Flavor | Good | Good | Lecithin smell acrid taste |

1) Determined by the phosphomolybdic acid method.

2) Determined by ICP.

3) In an iron frying pan (24cm) were placed an O/F composition (9g), Welsh onion (10g), and egg (40g), and heated. Subsequently cool cooked rice (300g) together with these were fried and then seasoned with table salt(1g) and soy (.5ml).

Reference Example 6

A natural oil or fat (75 parts by weight) was mixed with glycerin (25 parts by weight). To the mixture, calcium hydroxide (0.1 part by weight) was added, and then interesterification was carried out. The reaction product was subjected to molecular distillation to remove monoglycerides as much as possible. By this procedure, two diglyceride mixtures 1 and 2 were obtained at a yield of 40 parts, respectively.

Of the obtained diglyceride mixtures, respective compositions (% by weight), rising melting points ($^{\circ}\text{C}$), and contents of di-unsaturated diglycerides (% by weight) are shown in Table 8.

Table 8

| | | Mixture 1 | Mixture 2 |
|--|---------------|-----------|-----------------|
| Source | | Palm oil | Palm kernel oil |
| Composition (%) | Triglyceride | 20 | 18 |
| | Diglyceride | 78 | 80 |
| | Monoglyceride | 8 | 2 |
| Rising melting point ($^{\circ}\text{C}$) of diglyceride | | 46.2 | 57.2 |
| Rate of unsaturated fatty acid residues to total fatty acid residues in diglycerides | | 50.2 | 1.0 |
| Rising melting point ($^{\circ}\text{C}$) of diglyceride mixture | | 45.0 | 56.3 |
| Content (%) of unsaturated diglycerides in diglyceride mixture | | 20 | 0 |

Subsequently, with these glyceride mixtures, oils or fats (shown in Table 9) and solid fats and phospholipid mixtures (shown in Table 3), edible oil and/or fat compositions were prepared according to the following procedure: A glyceride mixture was mixed with an oil or fat and dissolved with heating to prepare homogenous oil or fat. To the resulting oil or fat, a solid fat and a phospholipid mixture were added to obtain an edible oil or fat.

Glyceride compositions and contents of unsaturated fatty acids of the thus-obtained edible oils or fats are given in Table 9.

Table 9

| Oil and/or fat compositions (Examples 9 through 15) | | | | | | | | |
|--|----------------------------------|------|------|------|------|------|------|------|
| Example | | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Oil and/or fat composition | DG mixture No. | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| | Parts by weight | 20 | 40 | 80 | 40 | 40 | 40 | 40 |
| | Hardened fish oil (MP 29° C) | 30 | | | 10 | | | |
| | Hardened fish oil (MP 35° C) | 40 | 50 | 40 | 50 | | | |
| | Hardened rapeseed oil (MP 24° C) | | | | | 10 | 20 | 20 |
| | Hardened rapeseed oil (MP 35° C) | | | | | 50 | | |
| Composition (%) | Rapeseed Shirashime oil | 10 | | | | | 40 | |
| | Trans-hard butter (MP 35° C) | | | | | | | 40 |
| | Cacao fat (MP 33° C) | | | | | | | |
| Composition (%) | Triglyceride | 83.6 | 87.2 | 50.8 | 66 | 67.2 | 67.2 | 67.2 |
| | Diglyceride | 16 | 32 | 48 | 28 | 32 | 32 | 32 |
| | Monoglyceride | 0.4 | 0.8 | 1.2 | 6.0 | 0.8 | 0.8 | 0.8 |
| Content of diunsaturated diglyceride in oil and/or composition | | 14.8 | 30 | 45 | 27.2 | 30 | 30 | 30 |
| Phospholipid mixture No.* | | 2 | 3 | 4 | 5 | 5 | 5 | 5 |

* Each number corresponds sample Nos. of phospholipid in Table 3. 5.0 wt.% of the phospholipid was used per the composition.

Each oil or fat composition (Example 9 through 15) in Table 9 was applied to a frying pan and tested for cooking characteristics in the same way as in Examples 7 and 8.

None of burning and sticking, smell on heating, spattering, and production of color was noted. Any obtained dish had very good taste and flavor.

Examples 16 to 18

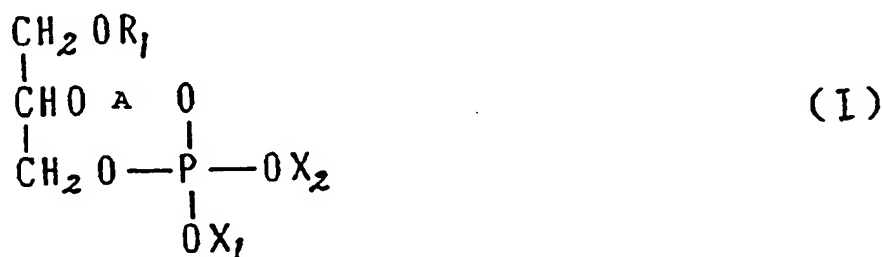
Twenty percent by weight of 99.5% ethyl alcohol was added to each of the compositions 1, 2, 3 of the invention and the control compositions 1, 2 and 3, shown in Table 2, to obtain compositions of the invention 16, 17 and 18 and then control compositions 5, 6 and 7, respectively. Each composition was determined in view of appearance at 10 degree C and then after stored for one week, a viscosity at 10 degree C and spraying property. The viscosity was determined with Rotovisco NV-St, a tradename of a rotor of HAAKE Company. The spraying property was determined by charging a pumping spray with each composition and spraying it at 10 degree C. Results are shown in Table 10. It is seen in the results that the compositions of the invention can be kept uniform and are good in storage, have a low viscosity of 32 to 40 cps and are good at spraying. The control compositions, on the other hand, offer separation from ethyl alcohol, have an undesirably high viscosity and are not good at spraying, merely giving a stream of liquid.

Table 10

| | invention | | | control | | |
|-------------------------------|-----------|----|----|---------------|----|----|
| | 16 | 17 | 18 | 5 | 6 | 7 |
| appearance at 10 degree C | uniform | | | ethyl alcohol | | |
| in 1 week | good | | | separated | | |
| viscosity (sp) at 10 degree C | 34 | 32 | 35 | 61 | 63 | 62 |
| spraying property 10 degree C | good | | | not good | | |

Claims

1. An edible oil and fat composition which comprises a phospholipid and a glyceride mixture comprising 5 to 100 percent by weight of a diglyceride, said phospholipid having the below shown formula (I) in which A is hydrogen or R₂, R₁ and R₂ each are an aliphatic acyl group, saturated or unsaturated, having 8 to 24 carbon atoms, X₁ is selected from the group consisting of base residues of choline, ethanolamine, serine, inositol and glycerol, hydrogen, an alkali metal, an alkaline earth metal, a trivalent metal and ammonium, and X₂ is selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal, a trivalent metal and ammonium and the phospholipid has a weight ratio of the phospholipid having no nitrogen in X₁ and X₂ to the phospholipid having nitrogen in X₁ and X₂ at a value of 1.0 or more.



2. A composition as claimed in Claim 1, which further comprises 0.1 to 50 percent by weight of ethyl alcohol.
3. A composition as claimed in Claim 1, in which
- the glyceride mixture comprises monoglycerides, diglycerides and triglycerides,
 - a weight ratio of the diglyceride to the monoglyceride ranges from 5:1 to 990:1,
 - the aliphatic acid (acyl) moieties in the glycerides have 8 to 24 carbon atoms.
4. A composition as claimed in Claim 1, in which
- the glyceride mixture comprises monoglycerides, diglycerides and triglycerides,
 - a weight ratio of the diglyceride to the monoglyceride ranges from 5:1 to 990:1,
 - the aliphatic acid (acyl) moieties in the glycerides have 8 to 24 carbon atoms, 70 percent by weight or above of unsaturated and
 - the diglycerides contains 40 percent by weight or more of diglycerides having unsaturated and saturated aliphatic acid moieties and 5 percent by weight or more of diglycerides having two saturated aliphatic acid moieties.
5. A composition as claimed in Claim 1, in which
- the glyceride mixture comprises monoglycerides, diglycerides and triglycerides,
 - a weight ratio of the diglyceride to the monoglyceride ranges from 5:1 to 990:1,
 - the aliphatic acid (acyl) moieties in the glycerides have 8 to 24 carbon atoms and comprises 70 percent by weight or above of unsaturated aliphatic acid moieties and
 - the diglycerides contains 40 percent by weight or lower of diglycerides having unsaturated and saturated aliphatic acid moieties and 5 percent by weight or lower of diglycerides having two saturated

aliphatic acid moieties.

6. A composition as claimed in Claim 5, which further comprises 0.1 to 50 percent by weight of ethyl alcohol.

7. A composition as claimed in Claim 1, which comprises 0.1 to 30 percent by weight of the phospholipid and 20 to 99.9 percent by weight of the glyceride mixture.

8. A composition as claimed in Claim 1, in which the phospholipid has a weight ratio of nitrogen to phosphorus in the range between zero and 0.20.

9. A composition as claimed in Claim 1, in which the phospholipid contains phosphatidic acid (PA) and/or a phosphatidic acid salt and lysophosphatidic acid (LPA) and/or a lysophosphatidic acid salt and a weight ratio of the sum total of the phosphatidic acid, a salt thereof, lysophosphatidic acid and a salt thereof to the sum total of phosphatidyl choline (PC) and phosphatidyl ethanolamine (PE) at a value of 1.0 or above.

10. An emulsion composition which comprises 50 to 99.9 wt.% of the composition as defined in Claim 1 and 0.1 to 50 wt.% of water.

15

20

25

30

35

40

45

50

55

19



Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number:

0 378 893 A3

12

EUROPEAN PATENT APPLICATION

21 Application number: 89303040.3

51 Int. Cl.⁵ **A23D 9/00**

22 Date of filing: 28.03.89

30 Priority: 17.01.89 JP 8151/89

43 Date of publication of application:
25.07.90 Bulletin 90/30

84 Designated Contracting States:
CH DE ES FR GB LI NL

88 Date of deferred publication of the search report:
27.03.91 Bulletin 91/13

71 Applicant: Kao Corporation
14-10, Nihonbashi Kayabacho 1-chome
Chuo-Ku Tokyo 103(JP)

72 Inventor: Yasukawa, Takuji
8762-23, Doaihoncho 1-chome
Hazaki-cho Kashima-gun Ibaraki(JP)
Inventor: Yasumura, Daisuke
8762-23, Doaihoncho 1-chome
Hazaki-cho Kashima-gun Ibaraki(JP)
Inventor: Yamasawa, Kimiko
9809-6, Doaihoncho 4-chome
Hazaki-cho Kashima-gun Ibaraki(JP)
Inventor: Tanaka, Yukitaka
8762-23, Doaihoncho, 1-chome
Hazaki-cho Kashima-gun Ibaraki(JP)
Inventor: Nishide, Tsutomu
8762-23, Doaihoncho, 1-chome
Hazaki-cho Kashima-gun Ibaraki(JP)

74 Representative: Bannerman, David Gardner et
al
Withers & Rogers 4 Dyer's Buildings Holborn
London, EC1N 2JT(GB)

54 Edible oil/fat compositions.

57 An edible oil and fat composition comprises a phospholipid and a glyceride mixture comprising 5 to 100 percent by weight of a diglyceride. The phospholipid is a decomposition product of natural lecithin. It is stable and suitable for food and a cooking oil.

EP 0 378 893 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 3040

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|--|--|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| Y | EP-A-0 171 112 (UNILEVER N.V.) * Complete document * | 1,3-5, 7-10 | A 23 D 9/00 A 23 J 7/00 |
| Y | EP-A-0 075 463 (KYOWA HAKKO KOGYO K.K.) * Abstract; page 1, line 8 - page 2, line 16; page 2, line 35 - page 12, line 28; examples 1-3; claims 9,10 * | 1,3-5, 7-10 | |
| Y | US-A-2 062 782 (A.K. EPSTEIN et al.) * Complete document * | 1,3-5,10 | |
| Y | US-A-2 089 470 (A.K. EPSTEIN et al.) * Complete document * | 1,3-5,10 | |
| Y | US-E-2 890 3 (R. ANEJA et al.) * Abstract; column 1, line 10 - column 4, line 2; column 6, lines 4-8; examples 1,3-7 * | 1 | |
| D,Y | US-A-3 896 975 (D.W. FOLLMER) * Column 2, lines 3-15; column 2, line 29 - column 3, line 49; column 5, line 58 - column 7, line 42; examples 1,3; claims 1,4,5,17 * | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| | | | A 23 D A 23 J |
| The present search report has been drawn up for all claims | | | |
| Place of search | | Date of completion of search | Examiner |
| The Hague | | 12 December 90 | FISCHER W.H.F. |
| CATEGORY OF CITED DOCUMENTS | | | |
| X: particularly relevant if taken alone | | E: earlier patent document, but published on, or after the filing date | |
| Y: particularly relevant if combined with another document of the same category | | D: document cited in the application | |
| A: technological background | | L: document cited for other reasons | |
| O: non-written disclosure | | | |
| P: intermediate document | | &: member of the same patent family, corresponding document | |
| T: theory or principle underlying the invention | | | |